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| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) | | | |
| a. electrochemistry, micellar effects b. high performance liquid chromatography c. surfactants, cleavable (destructible) d. surfactants, functionalized quaternary phosphonium e. turnover catalysts | | | |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) | | | |
| This Final Report summarizes the work performed under the contract noted above. Five different aspects of chemical reactivity in surfactant-based and other organized media were investigated. The first involved the synthesis and characterization of several functionalized quaternary phosphonium surfactants and an evaluation of their potential as turnover catalysts for the base- (continued on next page) | | | |

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20. Abstract (continued)

catalyzed hydrolysis of carbon and phosphorous esters. The second aspect included the synthesis and characterization of cleavable (destructible) surfactants. The third aspects involved the ability of micellar media to control the course of an electrochemical reaction in which there was competition between dimerization and further reduction of a free radical intermediate. The fourth aspect comprised the performance of organic reactions on reversed-phase high performance liquid chromatography (HPLC) columns. The fifth aspect entailed micellar/emulsion catalysis of reactions of substrates covalently attached to surfactants by labile linkages.

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Organic Synthesis and Catalysis in Microemulsions

Final Report

by

David A. Jaeger

February 2, 1988

U.S. Army Research Office

Contract No. DAAG29-84-K-0135

Department of Chemistry

University of Wyoming

Laramie, WY 82071

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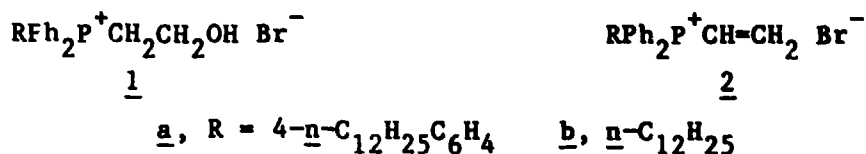
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I. Statement of the Problem Studied.

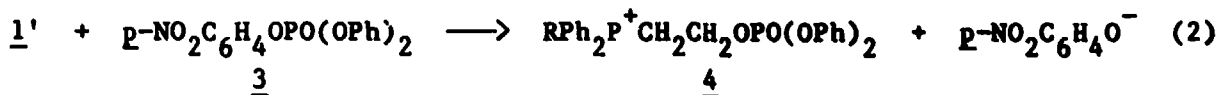
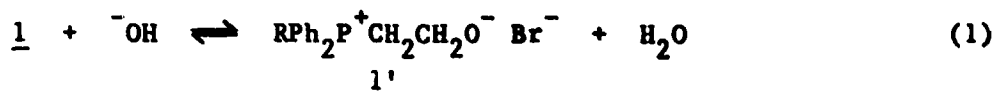
We have investigated several different aspects of chemical reactivity in surfactant-based and other organized media. The first involved the synthesis and characterization of several functionalized quaternary phosphonium surfactants and an evaluation of their potential as turnover catalysts for the base-catalyzed hydrolysis of carbon and phosphorous esters. The second aspect included the synthesis and characterization of cleavable (destructible) surfactants. The third aspect involved the ability of micellar media to control the course of an electrochemical reaction in which there was competition between dimerization and further reduction of a free radical intermediate. The fourth aspect comprised the performance of organic reactions on reversed-phase high performance liquid chromatography (HPLC) columns. The fifth aspect entailed micellar/emulsion catalysis of reactions of substrates covalently attached to surfactants by labile linkages.

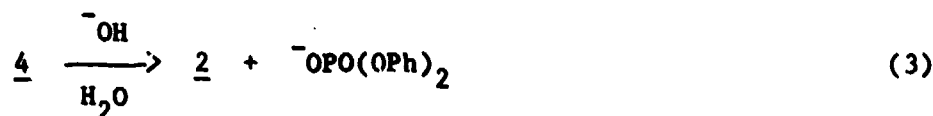
II. Statement of the Most Important Results.

In the first part of the project, functionalized quaternary phosphonium surfactants 1 and 2 were prepared, and 1a and 1b were evaluated as potential



turnover catalysts for the basic hydrolysis of p-nitrophenyl diphenyl phosphate (3) according to eq 1-4.¹ If eq 3 and 4 are faster than the formation of 4 (eq 2), 1 would indeed function as turnover catalysts.

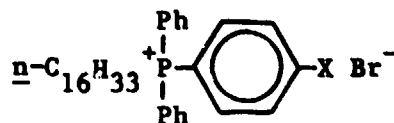




The catalytic abilities of 1 and 2 were studied in 0.01 M NaOH and in pH 10 borate buffer. In each case, k_{ψ}^1 was greater than k_{ψ}^2 . Thus, 1a and 1b did not function as turnover catalysts. However, the catalytic abilities of 1a are comparable to those of analogous functionalized quaternary ammonium surfactants in the hydrolysis of 3.¹

Vinyl phosphonium salts undergo reactions with OH^- in H_2O at C and P to give products of hydration and hydrolysis, respectively. In the above study, we found that 2 displayed unexpected C vs. P reactivity. In a separate study² with 2a, we found and delineated micellar effects on this competition that represent a vivid example of the ability of micelles to concentrate anionic reagents relative to the aqueous pseudophase. For bimolecular reactions, the usual consequences of such concentration are catalysis or inhibition. The results with 2a manifest a rare example of regiochemical consequences.

Also in the first part of the project, we prepared and characterized functionalized quaternary phosphonium surfactants 5 and 6.³ By UV and ^{31}P NMR methods 5 has a pK_a of 6.6. We evaluated the ability of 5 in comicellar

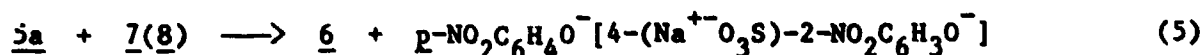


5, X = OH

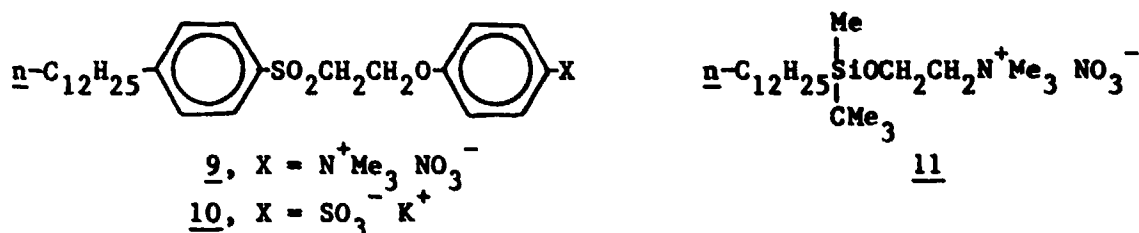
5a, X = O^-

6, X = OCOMe

form with hexadecyltrimethylammonium bromide (HTABr) to function as a turnover catalyst in the hydrolyses of p-nitrophenyl acetate (7) and sodium 4-acetoxy-3-nitrobenzenesulfonate (6) at pH 7 and 9 according to eq 5 and 6. At pH 9 with [5] = [HTABr] = 0.001 M, the rate of eq 5 with 7 was less than that of eq 6 with [6] = 0.0001 M and [HTABr] = 0.002 M. Thus, 5 functioned as a turnover catalyst.

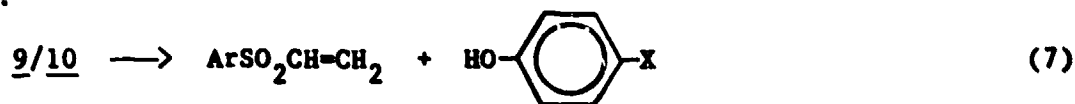


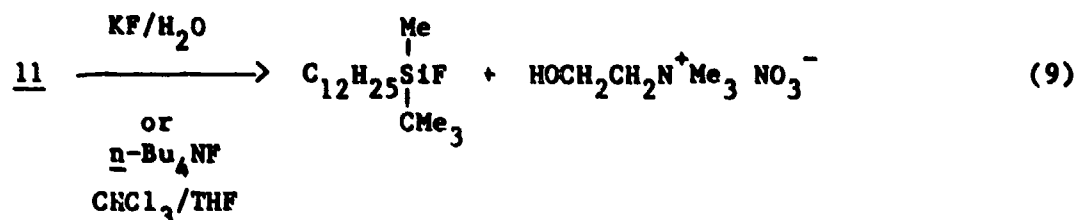
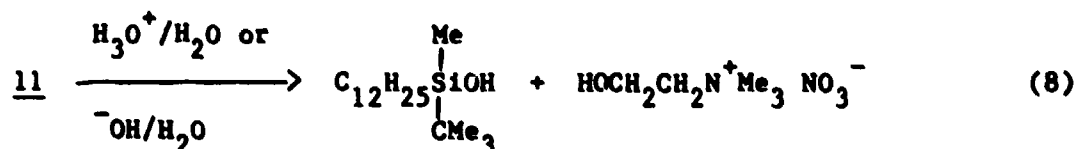
In the second part of the project we synthesized and characterized cleavable surfactants 9, 10, and 11.^{4,5} A cleavable surfactant contains an appropriate linkage that separates its major lipophilic and hydrophilic portions. The linkage is stable under certain conditions but labile under



others. Thus, a cleavable surfactant can be used as a catalyst for synthetic reactions under certain conditions, and then it can be converted to nonsurfactant compounds under other, generally mild conditions.

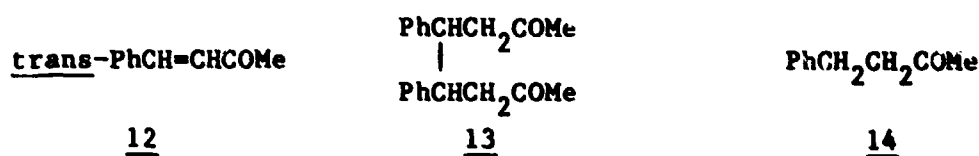
Straightforward isolation of desired products follows without the emulsion problems normally encountered with the use of regular surfactants. Compounds 9 and 10 are were labile with respect to E1cB elimination according to eq 7, and 11 with respect to cleavage of the silicon-oxygen bond according to eq 8 and 9.





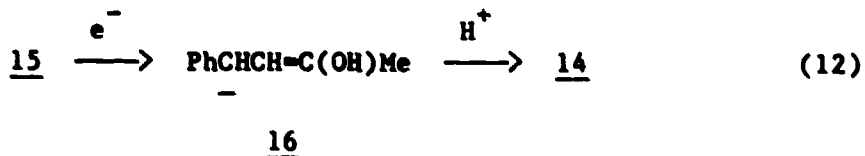
Both 9 and 10 were stable for 24 h in 0.1 M DCl at 75 °C. In D₂O alone at 25 °C, 9 slowly decomposed, and 10 was stable. At 25 °C, 9 decomposed completely within 10 min in 0.1 M NaHCO₃, whereas 10 was more stable in 0.1 M K₂CO₃. The difference in reactivities for 9 and 10 was attributed to a combination of micellar and electronic effects.⁴ At 25 °C in D₂O, 11 was stable for extended periods from pH 3 to 12, but hydrolyzed outside of this range. In H₂O and benzene-tetrahydrofuran, 11 was cleaved by KF and *n*-Bu₄F, respectively. As a micellar/emulsion or phase transfer catalyst, 11 was comparable to HTABr.⁵

The third part of the project involved a study^{6,7} of the electrochemical reduction of α,β-unsaturated ketone 12 at a Hg cathode in K₂O and in C₂H₅OH-H₂O. The effects of surfactants and various cations on E_{1/2} (I) and (II), and on the yields of 13 and 14 were delineated. The surfactants

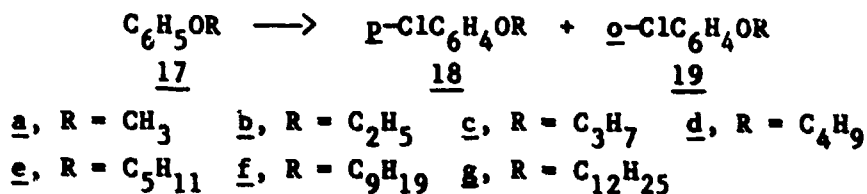


included HTABr, sodium dodecyl sulfate, and Brij 35, and the cations, Na⁺, K⁺, and Me₄N⁺. Products 13 and 14 result from the partitioning of free radical intermediate 15 between dimerization and further reduction, according to eq

10-12. Micellar effects and ion pairing to carbanion 16, derived from 15, facilitated the formation of 14 at the expense of 13.

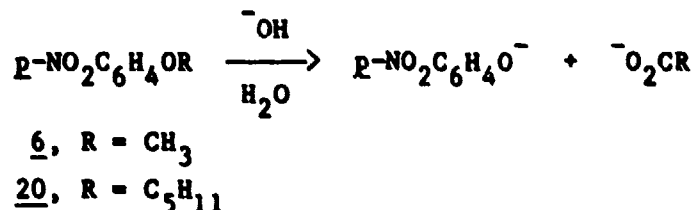


The fourth part of the project entailed the use of reversed-phase HPLC columns as chemical reactors for the reaction of water-insoluble organic substrates with water-soluble inorganic reagents. A series of *n*-alkyl phenyl ethers (17) was monochlorinated with chlorine water to give 18 and 19 under HPLC conditions in real-time on an alkylsilane-derivatized silica column.^{8,9} The para/ortho product ratios (18/19) obtained in the column reactions were greater than those obtained under homogeneous conditions in H₂O-MeCN. In competition runs of 17e vs. 17a, 17b, 17c, or 17d, only 17e reacted, and in runs of 17e vs. 17f, only 17f reacted, whereas 17f and 17g had comparable reactivities. The results demonstrated that a reversed-phase HPLC column can impart selectivity to reactions of compounds with the same intrinsic reactivity but different relative hydrophilic/lipophilic characters.

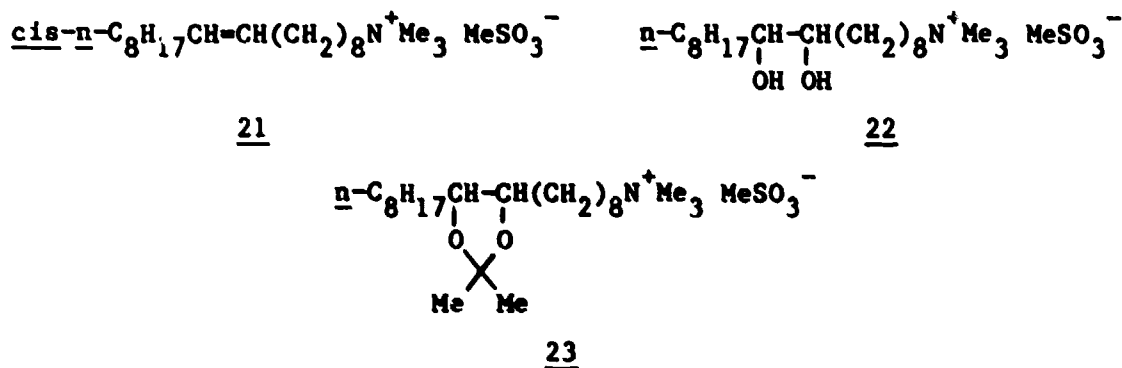


In another investigation,¹⁰ which we will complete shortly, the ⁻OH-catalyzed hydrolyses of 6 and *p*-nitrophenyl hexanoate (20) were performed on a reversed-phase column of macroporous 10-μm poly(styrene-divinylbenzene)

in real-time, and pseudo-first-order rate constants k_p were obtained. The maximum value of k_p^6/k_p^{20} was >25 , and the reactivity difference was attributed to different rates of desorption of 6 and 20 from the polymer surface into the mobile phase, wherein ^-OH was localized.



The fifth part of the project, which is still active, involved the synthesis and characterization of functionalized surfactants 21, 22, and 23. First, we will compare the micellar properties of these materials. Then 22 will be used as a micellar/emulsion catalyst for reactions of difunctional aldehydes/ketones covalently attached to it by an acetal/ketal linkage. After completion of a reaction, the linkage will be cleaved under mild acidic conditions to give the desired product with one functional group altered and the aldehyde/ketone group left intact. In such systems solubilization of the organic substrate by the surfactant aggregates does not simply depend on hydrophobic interactions, and as a result, greater concentrations of substrate can be obtained than otherwise possible.



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- (10) Jaeger, D. A.; Clennan, M. W., to be published.

III. Publications.

The publications under the contract correspond to references 1-9 above.

IV. Participating Scientific Personnel.

Principal Investigator:

David A. Jaeger

Postdoctoral Research Associates:

Durgadas Bolikal

Aloke K. Dutta

Graduate Students:

C. Timothy Finley (M.S., 1986)

M. W. Clennan

The views, opinions, and findings contained in this report are those of the author and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.